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(54) PROCESS FOR THE PRODUCTION OF RELIEF IMAGES

(71) We, AGFA-GEVAERT AKTIENGESELLSCHAFT, Leverkusen, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of relief images by the so-called ink jet process.

The term "ink jet process" is normally used to describe processes of recording visible images by spraying liquids such as coloured inks on to a substrate, the application of the coloured liquid being controlled by electric signals in accordance with the image. In these processes, which are suitable for the rapid recording of electric signals, for printing alpha-numeric characters or for point or line plotting of visible images, liquids are sprayed at a high pressure through a fine opening on a recording surface and the jet of small liquid droplets discharged from the opening can be electrically charged, deflected or atomized. In this way, the quantity of liquid applied to a particular area on the recording surface can be controlled by electric signals.

In this application, by the term ink jet process is meant the above process in which the jet need not be coloured and therefore need not necessarily produce a visible image. In other words the ink is any liquid, having the properties indicated below, and need not be coloured.

The transport of liquid from the opening of the nozzle to the recording surface in the form of jets of small droplets can also be achieved by the application of electrostatic forces at high voltages or by means of piezoelectrically produced compression waves or recoil forces or the forces on moving charges in a magnetic field. Particularly important in this connection is the process described in German Patent Specification No. 1,271,754, in which the droplets discharged from the fine nozzle become so highly charged by an electric field that the jet is atomized in the form of a cone.

This process is particularly suitable for the production of pictures because it makes it possible for the quantity of liquid reaching the recording surface to be continuously controlled and consequently the reproduction of continuous tone images can be controlled.

Recording processes operating on the ink jet principle have numerous advantages. Particularly to be mentioned is the extremely rapid and simple production of copies directly from an original. This obviates the time consuming exposure and photographic processing required in conventional photographic processes. Previously, however, relief images of the kind used in etching resists i.e. the non-etchable part of the etching resist or printing forms have not been obtained by the ink jet process. For these relief images, it was therefore still necessary to employ conventional photographic methods. These relief images are generally produced with the aid of layers of film-forming polymers which undergo a change in their solubility properties in the exposed areas. When the layers are subsequently treated with solvents, either the exposed or the unexposed areas may be dissolved out, depending on the nature of the material. Either a positive or a negative relief image of the original is then obtained.

It is among the objects of this invention to provide an ink jet process which may be used for the production of relief images.

We now have found a process for the production of a relief image by the ink jet method, in which an electrically controlled jet of liquid comprising a solution of a substance which is itself capable of altering the solubility properties of a polymer layer with respect to a given solvent or which contributes to the alteration of the solubility properties of a polymer layer with respect to a given solvent is sprayed on to a

polymer layer in conformity with the image areas so that the solubility properties of the polymer are modified in those areas which are encountered by the jet of solution, and this layer is then treated with said given solvent, so that a relief image of the original is obtained.

Relief images of excellent quality can be obtained by this process which does not require the usual photographic exposure and development and does not require the original to be optically suitable for copying. The process according to the invention is suitable, for example, for producing printing plates for the usual printing processes such as offset, relief or screen printing. The printing plates can be produced directly from facsimile signals. Moreover, purely synthetic patterns can be produced on printing plates, e.g. for textile printing, without the use of a drawing as original. The process according to the invention is also suitable for the production of printed circuits, which again do not require the usual original for copying, for example the printed circuits can be produced from patterns which have been synthesized or optimized in computers. The process according to the invention is, of course, suitable for all those purposes for which layers which are cross-linked or polymerized by light are used in conventional photographic processes.

The process according to the invention may be carried out in known ink jet apparatus, for example the apparatus described in US Patent Specifications No. 1,941,001; 2,143,376; 2,600,129; 2,512,743; 3,060,429; 3,298,030 and 3,373,437. The apparatus described by C. H. Hertz in German Patent Specification 1,271,754 and US Patent Specifications No. 3,416,153 and 3,673,601 is particularly suitable.

The solutions sprayed in the process according to the invention are preferably thin liquids and their electrical conductivity can easily be adapted to the requirements of the given apparatus so that no difficulties arise even when very fine spray nozzles are used.

If, in the process of the present invention, the particular ink jet process used is Hertz's process, the nozzle openings are preferably between 5 and 20 μm in diameter and the corresponding spray pressures between 10 and 50 atmospheres. The thickness of the polymer layer is preferably chosen so that it corresponds approximately to the depth of penetration of the droplets of solution which impinge upon it at high velocity. The thicknesses are preferably in the region of 0.1 to 10 μm, depending on the density and hardness of the polymer layer.

The disadvantages which occur in other possible processes of producing relief images on the ink jet principle are reduced or substantially obviated in the process according to the invention. Thus, for example, it is impossible in practice to spray etching reagents directly on to a substrate. The quantities of etching reagent which can be sprayed in this way are so small that only a very shallow etching could be obtained on the substrate. In addition, all parts of the apparatus which come into contact with the etching liquid, such as the nozzles, filters, valves, tubes and containers, must be resistant to corrosion. The employment of high pressures for etching reagents requires extensive and costly safety measures to eliminate risk of injury to the operating personnel.

The reverse method of spraying an etch resistant lacquer on to the substrate to produce a relief layer conforming to the image is also impossible in practice. Solutions of etching resistant polymers have a relatively high viscosity and it is therefore necessary to use nozzles with wide openings, which makes it impossible to produce relief images with sufficient resolving power. Moreover, most solvents have the disadvantage that they dry rapidly and thereby block the nozzles. It is in most cases necessary to use non-aqueous liquids which are not electrically conductive as solvents for such lacquer systems. It is therefore impossible to spray with apparatus which requires the sprayed liquid to have a finite conductivity, as in the case of the apparatus described in German Patent Specification No. 1,271,754. The addition of substances which improve the electrical conductivity, such as graphite particles, does not solve the problem because the relatively fine nozzles will only operate satisfactorily with homogeneous solutions.

The reduction in solubility of a polymer layer in areas conforming to the image generally comprises polymerization or cross-linking in the image areas or simply an imagewise change in the wetting properties of the polymer for the given solvent. The chemical structure of the polymer layer and the nature of the substance applied in the image areas by the process according to the invention to alter the solubility properties of the layer are only of secondary importance. In principle, any known combinations of polymers whose solubility is capable of being modified and substances which are capable of modifying the solubility properties can be used. Numerous systems of this kind are known. The choice of a suitable system, therefore, in general depends only on the desired nature of the relief layer and the purpose for which the relief image

produced by the process according to the invention is to be used.

Particularly important in this connection are those systems in which the substance which had been applied by spraying in accordance with the image produces a very rapid change in the solubility properties of the affected areas of the layer without any additional measures. Such systems include, for example, protein layers and in particular gelatin layers which can be cross-linked in the image areas by application of a solution of hardener by spraying so that when the protein is subsequently treated with a solvent or swelling agent such as water, only the untreated parts of the layer are removed. Many different hardeners for gelatin are known, particularly from the photographic art. Suitable hardeners include e.g. aqueous solutions of inorganic substances such as chromates and aluminium salts or zirconium salts, organic hardeners such as aldehydes, particularly aliphatic aldehydes such as formaldehyde, glycolaldehydes, glyoxal, glutaric aldehyde and acrolein crotonaldehydes, acids which contain aldehyde groups such as mucobromic acids or mucochloric acid, α- or γ-diketones, hydroxyketones, ethylene imine or ethylene oxide derivatives containing at least one epoxy group particularly substances which contain at least two such aldehyde groups, and trisacryloylhexahydrotriazine. The hardening reaction can be influenced in known manner by controlling the pH or the temperature, for example by maintaining the spraying solution at the required pH.

Layers which can be polymerized, cross-linked or dimerized in the image areas are also suitable for the process according to the invention. In these cases, a solution of the polymerization initiator, the cross-linking agent or the dimerizing agent is sprayed on to the layers in the areas conforming to the image. Numerous suitable systems are known also for this variation of the process. The reaction which takes place in the image areas of the layer can be accelerated by additional measures, e.g. by increasing the temperature or by uniform exposure to light. In the latter case, it is often sufficient to carry out the process in daylight, and, if indicated, polymerization or cross-linking may be accelerated by carrying out the process according to the invention in light of a suitable energy, e.g. UV light.

The layers which can be cross-linked may be, for example, layers of polyvinyl alcohol or of polymers with vinyl alcohol units, or cyclorubber, and the cross-linking agents sprayed on them may be solutions of organic azides, carbonyl azides or sulfonyl azides, particularly those of the benzene series. Systems of this kind have been described in U.S. Patent Specifications No. 2,852,379 and 3,467,518. Reference may also be made to U.S. Patent Specifications No. 2,687,958; 2,940,853; 3,092,494 and 3,143,423.

Suitable photopolymerizable layers have been described, for example, in U.S. Patent Specifications No. 2,670,286 and 2,760,863, Belgian Patent Specifications No. 782,600 and 783,846 and in U.S. Patent Applications Serial No. 247,757 and 256,162. According to the process of the invention, these polymerizable layers which generally contain vinyl groups are sprayed with suitable polymerization catalysts in the image areas. The polymerization reaction can be accelerated by uniform exposure to light during or after spraying.

Such polymerization initiators have been described in the works by J. C. Bloington "Radical Polymerization", Academic Press New York (1961). The following are examples of such compounds: Hydrazones; 5-membered heterocyclic rings which contain nitrogen; mercapto compounds; pyrylium or thiopyrylium salts; thiooxanthrones; dye-Redox systems; acridines or phenothiazines, e.g. according to German Offenlegungsschrift No. 2,027,467. The following are also suitable; Lophines (derivatives of Lophine i.e. 2, 4, 5-triphenylimidazole) e.g. according to British Patent Specifications No. 997,396 and 1,047,569; α-phenyl-ethyl alcohols; polynuclear quinones such as anthraquinone; 2-methyl anthraquinone; 2-tert.-butyl anthraquinone; anthraquinone-2-carboxylic acid butyl esters or phenanthrene quinones; benzophenone derivatives; e.g. according to British Patent Specification No. 1,242,988; or compounds of the benzoin series, such as benzoin; benzoin ether or hydroxymethylbenzoin. Reference may be made to U.S. Patent Specifications No. 3,639,321; 3,657,088; 3,607,693 and 3,636,026.

Systems in which the imagewise change in the solubility properties of the layer is effected by several components may also be used for the process according to the invention. In these cases, one of the hardening or cross-linking components may be introduced into the layer while the other component is sprayed on the layer in the image areas. Systems of this kind for hardening protein layers and in particular gelatin layers have been described, for example, in German Offenlegungsschrift No. 2,218,009.

Polymer layers whose solubility properties are altered by treatment with an acid are also suitable for the process according to the invention. In such cases, an aqueous acid is sprayed on the image

areas of the layer by the ink jet process. Numerous polymers which are cross-linked by acids are known, for example the commercial alkyd resins of polyvalent alcohols and acids. Polymers which contain N-methylol-ether groups are also suitable, e.g. the systems described in German Patent Specifications No. 1,622,764 and 1,447,592. When the layers described in the said Patent Specifications are used for the process according to the invention, the compound which splits off acid is not used and the layers are only treated with acid in the image areas in accordance with the present invention. Reference is also made to the polymers mentioned in U.S. Patent Specifications No. 2,966,481 and 2,984,588.

The agents applied may make the binding agent of the layer insoluble or they may have the opposite effect. Layers which are not soluble or swellable in a predetermined solvent can be made soluble by imagewise spraying with suitable compounds. For example, if a hardened gelatin layer, hardened for example with formaldehyde, which is not soluble or removable with water under reasonable conditions is treated imagewise with a proteolytic ferment such as trypsin, biolase or bioprase the gelatine is degraded and becomes water-soluble.

Phenol formaldehyde resins may also be used as receptor layers and they may be sprayed with a solution of quinone diazides such as those described in U.S. Patent Specification No. 3,046,118. When the receptor layer is subsequently treated with aqueous alkali, the parts of the layer on which the quinone diazide has been sprayed can be dissolved out. A negative relief of the original is then obtained.

Example 1

A gelatin layer which contained 10 ml of a 5% aqueous solution of the sodium salt of *p*-isocyanatobutyric acid per kg of gelatin was applied to a polyethylene terephthalate substrate. The gelatin layer had a thickness of about 4 μm after drying.

A 3% aqueous formaldehyde solution to which 0.5% of a water-soluble dye had been added to render it visible was then sprayed on to this layer in the image areas by Hertz's ink jet process according to German Patent Specification No. 1,271,754. The spray pressure was 30 atmospheres gauge, the scanning velocity was 3 m/s.

The originals used for producing the electric signals for controlling the jet of droplets in conformity with the image were reflection copies which were scanned photo-electrically.

The receptor material containing the layer which was to be modified by the spray was stretched over a rotary cylinder which was rigidly connected to a second cylinder on which was mounted the original copy which was to be scanned. The scanning velocity, i.e. the velocity with which the receptor surface moved past the nozzle, could be varied by adjusting the speed of rotation of the cylinders. The rate of feed of the scanning head and spray nozzle in the direction parallel to the axis of the cylinder was adjusted to produce 10 scan lines per mm.

The formaldehyde solution was forced through a nozzle with an internal diameter of 7 μm and controlled with signal voltages of between 0 and 800 volt.

10 minutes after spraying, the receptor material was sprayed with hot water (50°C) or bathed in hot water for 30 seconds in a developer dish. Those areas of the gelatin layer which had not been struck by droplets of formaldehyde were dissolved out by the water. A relief image of hardened gelatin remained behind on the polyester foil.

Example 2

Instead of the polyester substrate used in Example 1, the copper surface of a copper-coated hard paper foil (Supra Carta copper quality 96 DLS, Isola-Werke, Dueren) of the type normally used for producing printed circuits was coated with the gelatin layer described in Example 1 (thickness of gelatin layer after drying 5 μm: thickness of copper layer 35 μm). The formaldehyde solution was sprayed on the receptor surface under the same conditions as in Example 1. The areas of the gelatin layer which had not been struck by formaldehyde solution and hardened were washed out with water. A relief layer of hardened gelatin was left behind on the copper layer. The foil was then bathed for 60 minutes in a 44% Fe-III chloride solution. This dissolved out the copper in the exposed areas. The hardened gelatin was sufficiently softened in this bath so that it could subsequently be washed off with hot water. A metal relief which represented a positive copy of the scanned original was left behind on the insulating substrate (hard paper). Instead of a positive copy, a negative copy of the original can be produced by connecting a reversing stage into the electronic signal amplifier.

Example 3

A layer of acid-hardened clear lacquer 5 μm in thickness was applied to the copper side of a copper-coated hard paper foil of the type described in Example 2. The lacquer comprised a mixture of equal parts by weight of an alkyd resin based on phthalic acid anhydride/benzoic acid and polyhydric alcohols such as pentaerythritol

and trimethylolpropane and unsaturated higher fatty acid esters such as castor oil and soya oil and an urea formaldehyde resin, e.g. the product marketed by BASF AG under the trade name Plastopal EBS 100.

To produce the coating, 1 part by weight of the resin mixture was dissolved in 2 parts by weight of methyl ethyl ketone and the solution was applied to the cleaned copper surface. After drying (30 minutes at 35°C), the layer was sprayed imagewise with an approximately 1% solution of p-toluene sulfonic acid in dimethylformamide at a pressure of 40 atmospheres and a scanning velocity of 3 m/s. The hardening in the image areas initiated in this way was completed by a heat treatment at a temperature of 75°C for 10 minutes. The surface elements of the lacquer layer which had been left untreated and therefore not hardened were dissolved out by bathing in methyl ethyl ketone. The hardened image elements formed a protective layer which was carried out as described in Example 2.

Example 4

A copper foil was coated with a 5 μm thick gelatin layer as described in Example 2 but this gelatin layer contained formaldehyde solution as hardener. A 0.75% aqueous solution of trypsin adjusted to a pH of 7.5 was sprayed on the gelatin layer (spray pressure 40 excess atmosphere; nozzle diameter 10 μm; scanning velocity 3 m/s). When the trypsin solution had acted on the layer for about 15 minutes, the foil was bathed in water at 40°C. The hardened gelatin had been degraded in the areas which were struck by the spray and had therefore become water-soluble. An image in the form of a gelatin relief was left on the copper surface to serve as resist for the etching process described in Example 2.

WHAT WE CLAIM IS:—

1. A process for the production of a relief image by the ink jet process in which an electrically controlled jet of liquid comprising a solution of a substance which is itself capable of altering the solubility properties of a polymer layer with respect to a given solvent or which contributes to the alteration of the solubility properties of a polymer layer with respect to a given solvent is sprayed on to a polymer layer in conformity with the image areas so that the solubility properties of the polymer are modified in those areas which are encountered by the jet of solution and this layer is then treated with said given solvent so that a relief image of the original is obtained.

2. A process as claimed in claim 1 which is carried out in an apparatus provided with nozzles with openings between 5 and 20 μm to produce the jet and operated at a spray pressure of from 10 to 50 atmospheres.

3. A process as claimed in claim 1 or claim 2 in which the thickness of the polymer layer corresponds approximately to the depth of the pentration of the droplets of the jet which impinge upon it.

4. A process as claimed in any of claims 1 to 3 in which the thickness of the polymer layer is from 0.1 to 10 μm.

5. A process as claimed in any of claims 1 to 4 in which the polymer layer is a protein layer which is sprayed with a solution of a hardener.

6. A process as claimed in claim 5 in which the protein is gelatin.

7. A process as claimed in claim 5 or claim 6 in which the hardener is a chromate, an aluminium or zirconium salt, an aldehyde, an acid which contains aldehyde groups, α- or γ-diketone, a hydroxyketone, an ethylene imine or ethylene oxide derivative containing at least one epoxy group or trisacroylhexahydrotriazine.

8. A process as claimed in any of claims 1 to 4 in which the polymer layer is a layer of polyvinyl alcohol, a polymer with vinyl alcohol units or a cyclorubber which is sprayed with a cross linking agent.

9. A process as claimed in claim 8 in which the cross linking agent is a solution of an organic azide, carbonyl azide or sulphonyl azide.

10. A process as claimed in any of claims 1 to 4 in which the polymer layer is a photopolymerisable layer which is sprayed with a polymerisation initiator.

11. A process as claimed in claim 1 substantially as herein described with reference to any of the Examples.

12. A relief image when produced by a process as claimed in any of claims 1 to 11.

13. A printing plate or printed circuit which comprises a relief image as claimed in claimed 12.

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